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(54) Title: HIGH ETCH SELECTIVITY ETCHANT FOR DOPED SILICATE GLASS

(57) Abstract: An etchant for highly selective etching of silicon-based materials. The etchant comprises sulfuric acid and hydrofluoric acid with low water content.

HIGH ETCH SELECTIVITY ETCHANT FOR DOPED SILICATE GLASS

Field Of Invention

The invention generally relates to semiconductor device fabrication and, more particularly, to providing highly selective etching of silicon based oxides.

Background Of Invention

In device fabrication, device layers of insulating, semiconducting, and conducting materials are formed on a substrate. The layers are patterned to create features and spaces. The features and spaces are patterned so as to form devices, such as transistors, capacitors, and resistors. These devices are then interconnected to achieve a desired electrical function, creating an integrated circuit (IC).

The ability to selectively etch or remove specific layers without attacking others facilitates patterning of the device layers. Etch selectivity is defined as the ratio of etch rates between a first material that is to be etched with respect to a second material. Of particular interest is the selectivity of silicon-based materials. Silicon-based materials such as silicon-based oxides are generally employed as, for example, dielectric layers, masks for etch processes as well as etch stop and

polish stop layers. Conventional wet etch processes employs a fluoride-based etchant to etch silicon-based materials. Such etchants produce an etch selectivity of less than 15:1.

As device dimension decreases and complexity increases in the advance IC designs, it is becoming more important to have high selectivity between different types of silicon-based materials. Typically, the etch selectivity of different silicon-based materials required in advance IC designs exceeds that achievable with conventional wet etch processes. This results in reduced manufacturing yields or the loss of process capability at all. On the other hand very high selectivities offer new possibilities in process architecture.

From the above discussion, it is desirable to provide an etch system for silicon based oxides with high etch selectivity for advance IC designs.

Summary of the Invention

The invention relates to a highly selective etching of silicon-based materials. In one embodiment, an etchant comprising sulfuric acid and hydrofluoric acid having a low water content is used for to etch a doped silicate glass with a high selectivity to silicon-based materials such as silicon oxides, silicon nitrides,

silicate glass, or polysilicon. The water content of the etchant is less than 20% by volume.

Description of the Invention

The invention relates generally to semiconductor fabrication and particularly to an etchant that provides a high etch selectivity of a first material to a second material on a substrate such as a semiconductor wafer. The first and second materials, in one embodiment, are silicon-based materials. The silicon-based materials can be formed by techniques such as thermal oxidation, chemical vapor deposition (CVD), or a combination of thermal oxidation and CVD.

In one embodiment, the first material comprises a doped silicate glass. Dopants such as boron, phosphorus, or arsenic, are useful to dope the silicate glass. In one embodiment, the doped silicate glass comprises, for example boron such as borosilicate glass (BSG). Other types of doped silicate glass such as phosphosilicate glass (PSG) are also useful. A doped silicate glass comprising more than one type of dopant, such as borophosphosilicate glass (BPSG) is also useful. Including other types of dopants, such as phosphorous (P) or arsenic (A), in the doped silicate glass is also useful. The second silicon-based material comprises

silicon oxide, silicon nitride, undoped silicate glass or polysilicon. The polysilicon can be doped or undoped. In one embodiment, the second silicon-based material comprises silicon oxide. The silicon-based oxide is formed by thermal oxidation. The etch system etches the doped silicate glass with an etch selectivity to the silicon oxide of greater than about 15:1, preferably greater than about 40:1, more preferably greater than about 70:1, and even more preferably greater than about 100:1.

In accordance with one embodiment of the invention, the etchant comprises sulfuric acid and hydrofluoric acid having a low water content to produce a high etch selectivity between silicon-based materials. In one embodiment, the etch system comprises a water content of less than about 20% by volume, preferably less than about 15% by volume, more preferably less than about 10% by volume, and even more preferably less than about 5% by volume.

The high etch selectivity can be achieved using a wide range of mixing ratio of concentrated sulfuric acid and concentrated hydrofluoric acid. The ratio of the acids affect the etch rate. A higher ratio of sulfuric acid causes the etchant to etch at a lower etch rate and vice-versa. Although the ratio of sulfuric acid and

hydrofluoric acid changes actual etch rates of the materials being etched, the etchant retains its high etch selectivity characteristics. In one embodiment, the etchant comprises sulfuric acid and hydrofluoric acid in a ratio of about 5:1 to about 20:1 by volume. A ratio of greater than 20:1 can also be useful if lower etch rates are desired.

The substrate is exposed to the etchant using wet etch tools, such as a bath, a spray tool or a spintech tool. The etchant exhibits high etch selectivity characteristics over a wide range of temperatures. For example, the etchant can be used at temperatures ranging from below room temperature to above 80°C with a high etch selectivity. The temperature, however, does affect the etch rates of the materials. As such, the temperature of the etch can be chosen to produce the desired etch rates on the materials while still retaining the desired high etch selectivity property.

The etch rate of the doped silicate glass can be controlled by changing the concentration of the dopants. In particular, the etch rate can be increased or decreased by increasing or decreasing the dopant concentration, respectively, in the doped silicate glass. In one embodiment, the doped silicate glass comprises a dopant concentration of at least 3 wt%. A dopant

concentration of about 3 - 3.5 wt% has been found to produce an etch selectivity to silicon oxide of about 45:1. Increasing the dopant concentration of the doped silicate glass to above 5 wt% produces an etch selectivity to silicon oxide of greater than about 70:1. In one embodiment, the BSG comprises a concentration of B of at least 3 wt%, preferably greater than about 5 wt%.

Example

An etchant comprising a mixture of 5 parts sulfuric acid (96%) and 1 part hydrofluoric acid (49%) was used to etch a BSG layer comprising 5 wt% B and a thermal oxide layer. The etchant yielded an etch rate of about 720 nm/min for the BSG layer and only 14 nm/min for the thermal oxide layer, resulting in an etch selectivity of the BSG to the thermal oxide of about 51:1.

While the invention has been particularly shown and described with reference to various embodiments, it will be recognized by those skilled in the art that modifications and changes may be made to the present invention without departing from the scope thereof. The scope of the invention should therefore be determined not with reference to the above description but with reference to the appended claims along with their full scope of equivalents.

What is claim d is:

1. An etchant comprising sulfuric acid and hydrofluoric acid with a low water content to produce a high etch selectivity.

2. The etchant of claim 1 wherein the first material comprises a doped silicate glass and the second material comprises a silicon-based material.

3. The etchant of claim 2 wherein the first material comprises a doped silicate glass and the second material comprises a silicon-based material selected from the consisting of polysilicon, silicate glass, silicon oxide, or silicon nitride.

4. The etchant of claim 3 wherein the doped silicate glass comprises a dopant concentration of greater than 3 wt%.

5. The etchant of claim 4 wherein the water content is less than about 20% by volume.

6. The etchant of claim 4 wherein the water content is less than about 15% by volume.

7. The etchant of claim 4 wherein the water content is less than about 10% by volume.

8. The etchant of claim 4 wherein the water content is less than about 5% by volume.

9. The etchant of claim 3 wherein the doped silicate glass comprises a dopant concentration of greater than 5 wt%.

10. The etchant of claim 9 wherein the water content is less than about 20% by volume.

11. The etchant of claim 9 wherein the water content is less than about 15% by volume.

12. The etchant of claim 9 wherein the water content is less than about 10% by volume.

13. The etchant of claim 9 wherein the water content is less than about 5% by volume.

14. The etchant of claim 3 wherein the doped silicate glass comprises boron.

15. The etchant of claim wherein the doped silicate glass comprises a boron concentration of greater than 3 wt%.

16. The etchant of claim 15 wherein the water content is less than about 20% by volume.

17. The etchant of claim 15 wherein the water content is less than about 15% by volume.

18. The etchant of claim 15 wherein the water content is less than about 10% by volume.

19. The etchant of claim 15 wherein the water content is less than about 5% by volume.

20. The etchant of claim wherein the doped silicate glass comprises a boron concentration of greater than 5 wt%.

21. The etchant of claim 20 wherein the water content is less than about 20% by volume.

22. The etchant of claim 20 wherein the water content is less than about 15% by volume.

23. The etchant of claim 20 wherein the water content is less than about 10% by volume.

24. The etchant of claim 20 wherein the water content is less than about 5% by volume.

25. The etchant of claim 2 wherein the water content is less than about 20% by volume.

26. The etchant of claim 2 wherein the water content is less than about 15% by volume.

27. The etchant of claim 2 wherein the water content is less than about 10% by volume.

28. The etchant of claim 2 wherein the water content is less than about 5% by volume.

29. The etchant of claim 25 wherein the high etch selectivity of the first material to the second material is greater than 15:1

30. The etchant of claim 25 wherein the high etch selectivity of the first material to the second material

is greater than 45:1

31. The etchant of claim 25 wherein the high etch selectivity of the first material to the second material is greater than 70:1

32. The etchant of claim 25 wherein the high etch selectivity of the first material to the second material is greater than 100:1

33. A method for wet etching comprising:

providing a substrate including first and second materials; and

exposing the substrate to an etchant comprising sulfuric acid and hydrofluoric acid with a low water content, the etching etches the first material with a high etch selectivity to the second material.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/311

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 0 989 598 A (SIEMENS AG) 29 March 2000 (2000-03-29) column 1, line 8 - line 34 column 1, line 52 -column 2, line 13 column 2, line 26 - line 41 column 3, line 11 - line 13 column 3, line 34 - line 53 column 4, line 31 - line 45; figure 1 column 5, line 18 - line 25; figure 2 column 5, line 43 -column 6, line 1 ---	1-33
P,X	DE 198 50 838 A (SIEMENS AG ;MOSEL VITELIC INC (TW); PROMOS TECHNOLOGIES INC (TW)) 23 March 2000 (2000-03-23) page 2, line 3 - line 5 page 2, line 40 - line 62 page 3, line 3 - line 45; tables 1-3 --- -/--	1-3,33

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 932 187 A (SIEMENS AG ;TOKYO SHIBAURA ELECTRIC CO (JP); IBM (US)) 28 July 1999 (1999-07-28) column 2, line 7 - line 51 column 4, line 5 - line 15; figure 1 column 5, line 3 - line 11 column 6, line 22 - line 35	1-28,33
X	US 5 300 463 A (CATHEY DAVID A ET AL) 5 April 1994 (1994-04-05) column 1, line 8 - line 38 column 1, line 59 -column 2, line 60; claims 8-15	1-3,33
Y		4,9,14, 15,19
A		5-8, 10-13, 16-18, 20-32
Y	US 3 751 314 A (RANKEL L) 7 August 1973 (1973-08-07) column 1, line 59 -column 2, line 23 column 2, line 31 - line 45; figures 1,2 column 2, line 62 -column 3, line 26; figure 3 column 3, line 61 -column 4, line 16	4,9,14, 15,19
A		1-3
X	US 4 465 549 A (RITZMAN IRA G) 14 August 1984 (1984-08-14) column 2, line 52 - line 67 column 3, line 47 -column 4, line 31; figure 4	1,33
A		2,3, 25-32

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/25481

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0989598 A	29-03-2000	DE 19844102 A	06-04-2000
DE 19850838 A	23-03-2000	US 6123865 A	26-09-2000
EP 0932187 A	28-07-1999	CN 1230018 A JP 11265982 A	29-09-1999 28-09-1999
US 5300463 A	05-04-1994	NONE	
US 3751314 A	07-08-1973	NONE	
US 4465549 A	14-08-1984	NONE	